

## PATENT ABSTRACTS OF JAPAN

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(30)Priority

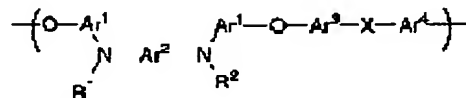
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## (54) ORGANIC ELECTROLUMINESCENT ELEMENT

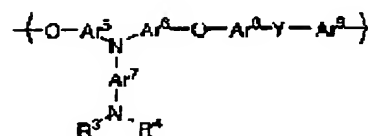
(57)Abstract:

PROBLEM TO BE SOLVED: To enable low-voltage drive while improving light emitting efficiency, and improve heat resistance by including aromatic diamine-contained polyether having specified weight average molecular weight and the structure and an electron acceptable compound in a hole injection layer.

SOLUTION: Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup>, Ar<sup>4</sup>, Ar<sup>5</sup>, Ar<sup>6</sup>, Ar<sup>7</sup>, Ar<sup>8</sup>, Ar<sup>9</sup> means separate divalent aromatic cyclic residue capable of having a substituent group, and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> means aromatic cyclic group capable of having a substituent group or aromatic heterocyclic group, X and Y means direct bonding or connecting group expressed with formula III and having a repetition unit expressed with formulas I, II, and the electron acceptable compound is included in the aromatic diamine contained polyether having 1,000-1,000,000 of weight average molecular weight so as to form a hole injection layer of the light emitting element. Hole is generated by the movement of electric charge so as to improve the electrical conductivity, and electrical bond between the light emitting layer and the positive electrode is improved so that the drive voltage can be set low, and while stability in the case of continuous drive is improved.



I



II



III

## LEGAL STATUS

[Date of request for examination]

13.03.2003

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

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[Date of extinction of right]

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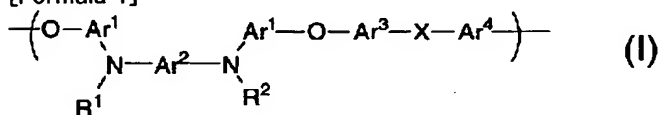
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## CLAIMS

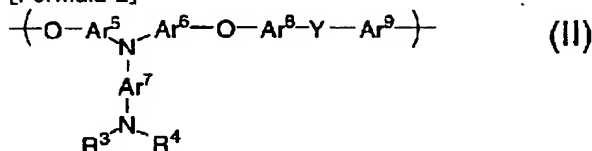
## [Claim(s)]

[Claim 1] Organic electroluminescence devices to which this hole injection layer is characterized by having the repeat unit expressed with the following general formula (I) or (II), and containing the aromatic series diamine content polyether whose weight average molecular weight is 1,000-1,000,000, and an electronic receptiveness compound in the organic electroluminescence devices by which the hole injection layer was formed between this luminous layer and the anode plate while the luminous layer pinched by an anode plate and cathode is formed on a substrate.

## [Formula 1]

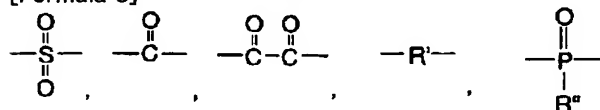


## [Formula 2]



(Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup>, Ar<sup>4</sup>, Ar<sup>5</sup>, Ar<sup>6</sup>, Ar<sup>7</sup>, Ar<sup>8</sup>, and Ar<sup>9</sup> show among a formula the divalent aromatic series ring residue which may have the substituent respectively independently, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> show the aromatic series ring machine or aromatic heterocycle radical which may have the substituent, and X and Y are chosen from direct coupling or the following connection radical.)

## [Formula 3]

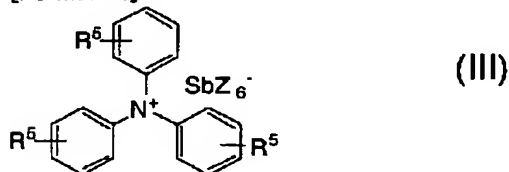


(R' shows among a formula the alkylene group which may have the substituent, and R'' of aromatic series ring machines which may have the alkyl group or the substituent is shown.)

[Claim 2] Organic electroluminescence devices according to claim 1 which the value which lengthened the electron affinity of said electronic receptiveness compound from the ionization potential of said aromatic series diamine content polyether is 0.7eV or less, and are characterized by the content of this electronic receptiveness compound in said hole injection layer being 0.1 - 50% of the weight of the range to this aromatic series diamine content polyether.

[Claim 3] Organic electroluminescence devices according to claim 1 or 2 characterized by said electronic receptiveness compound being at least one sort of a compound expressed with the following general formula (III).

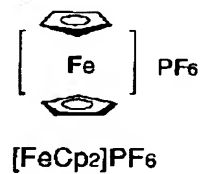
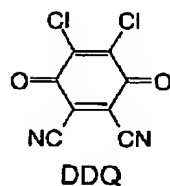
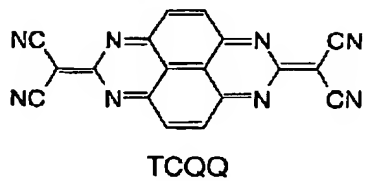
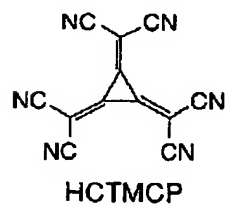
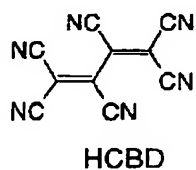
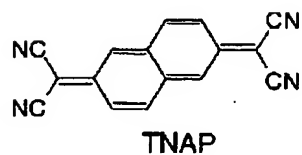
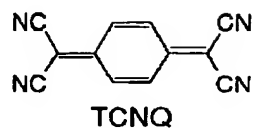
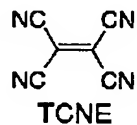
## [Formula 4]



(Z shows a halogen atom among a formula and R<sup>5</sup> shows the alkyl group, cyano group, or nitro group which may have the hydrogen atom, the halogen atom, and the substituent.)

[Claim 4] Organic electroluminescence devices according to claim 1 or 2 characterized by said electronic receptiveness compound being at least one sort chosen from the following compound group.

## [Formula 5]



[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the thin film mold device which emits light, applying electric field to the luminous layer which consists of an organic compound in detail about organic electroluminescence devices.

[0002]

[Description of the Prior Art] Although what doped Mn which is an emission center, and rare earth elements (Eu, Ce, Tb, Sm, etc.) is common to ZnS, CaS, SrS, etc. which are the II-VI group compound semiconductor of an inorganic material as an electroluminescence (EL) component of a thin film mold conventionally As for the EL element produced from the above-mentioned inorganic material, 1 alternating current drive has [ the need (generally 50-1000Hz) and 2 driver voltage ] the trouble which has a problem difficult [ the high (about / Generally 200 / V) formation of 3 full color ], and especially blue that the cost of 4 circumference drive circuits is high.

[0003] However, development of the EL element using an organic thin film came to be performed in recent years for amelioration of the above-mentioned trouble. In order to raise luminous efficiency especially, the class of electrode is optimized for the purpose of the improvement in effectiveness of the carrier impregnation from an electrode. By development (Appl.Phys.Lett., 51 volumes, 913 pages, 1987) of the organic electroluminescence devices which prepared the electron hole transportation layer which consists of aromatic series diamine, and the luminous layer which consists of the aluminum complex of 8-hydroxyquinoline

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to the thin film mold device which emits light, applying electric field to the luminous layer which consists of an organic compound in detail about organic electroluminescence devices.

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[Translation done.]

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PRIOR ART

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[Description of the Prior Art] Although what doped Mn which is an emission center, and rare earth elements (Eu, Ce, Tb, Sm, etc.) is common to ZnS, CaS, SrS, etc. which are the II-VI group compound semiconductor of an inorganic material as an electroluminescence (EL) component of a thin film mold conventionally As for the EL element produced from the above-mentioned inorganic material, 1 alternating current drive has [ the need (generally 50-1000Hz) and 2 driver voltage ] the trouble which has a problem difficult [ the high (about / Generally 200 / V) formation of 3 full color ], and especially blue that the cost of 4 circumference drive circuits is high.

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EFFECT OF THE INVENTION

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[Effect of the Invention] According to the organic electroluminescence devices of this invention in which the hole injection layer containing a specific aromatic series diamine content polyether and a specific electronic receptiveness compound was formed, a high luminous efficiency drive, by the low battery is possible, and, moreover, a component with good thermal resistance is offered as explained in full detail above.

[0107] Therefore, the technical value is large as a display device for mount as which the organic electroluminescence devices by this invention can consider the application to the light source (for example, the light source of a copying machine, the back light light source of a liquid crystal display or instruments) which employed the description as a flat-panel display (for example, the object for OA computers and a flat TV), or a field illuminant efficiently, the plotting board, and a beacon light to be, and high thermal resistance is required especially.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, in the approach of inserting a hole injection layer between an anode plate and an electron hole transportation layer, when a porphyrin derivative and a phthalocyanine compound are used as a hole injection layer, a spectrum changes for the light absorption by these film itself, or there is a problem of becoming less transparent [ carry out exterior coloring and ].

[0009] In a star bust mold aromatic series triamine, hydrazone compound, aromatic series diamine derivative [ of an alkoxy permutation ], p-(9-anthryl)-N, and N-G p-tolyl aniline, since the advantage that ionization potential is low and transparency is good has low glass transition point and melting point of a certain thing, it is inferior to thermal resistance, and the stability over partial heating at the time of a continuation drive is bad, and a brightness fall and a power surge become a problem.

[0010] On the other hand, there is that no polymer system ingredients, such as poly thienylene vinylene, Polly p-phenylenevinylene, and the poly aniline, report low-battery-izing of driver voltage and an improvement of a drive life.

[0011] It is the big problems as the light source of the back light of facsimile, a copying machine, and a liquid crystal display etc. that the electrical potential difference at the time of the drive of organic electroluminescence devices is high and that stability including thermal resistance is low, and they are not especially desirable as display devices, such as a full color flat panel display.

[0012] Therefore, this invention can be made to drive with a low battery and high luminous efficiency, and has good thermal resistance, and aims at offering the organic electroluminescence devices which can continue at a long period of time and can maintain a stable luminescence property.

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[Translation done.]

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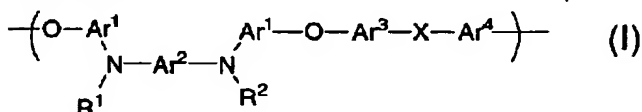
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## MEANS

[Means for Solving the Problem] The organic electroluminescence devices of this invention are characterized by for this hole injection layer having the repeat unit expressed with the following general formula (I) or (II), and containing the aromatic series diamine content polyether whose weight average molecular weight is 1,000-1,000,000, and an electronic receptiveness compound in the organic electroluminescence devices by which the hole injection layer was formed between this luminous layer and the anode plate while the luminous layer pinched by an anode plate and cathode is formed on a substrate.

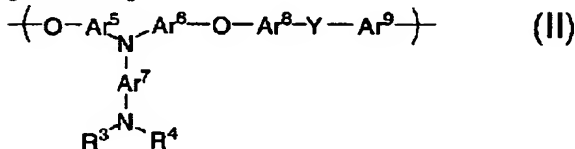
[0014]

[Formula 6]



[0015]

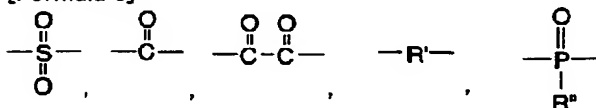
[Formula 7]



[0016] (Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup>, Ar<sup>4</sup>, Ar<sup>5</sup>, Ar<sup>6</sup>, Ar<sup>7</sup>, Ar<sup>8</sup>, and Ar<sup>9</sup> show among a formula the divalent aromatic series ring residue which may have the substituent respectively independently, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> show the aromatic series ring machine or aromatic heterocycle radical which may have the substituent, and X and Y are chosen from direct coupling or the following connection radical.)

[0017]

[Formula 8]



[0018] (R' shows among a formula the alkylene group which may have the substituent, and R'' of aromatic series ring machines which may have the alkyl group or the substituent is shown.)

Namely, the result wholeheartedly examined so that this invention persons may offer the organic electroluminescence devices which solve the conventional trouble and can maintain a stable luminescence property in an elevated temperature. In the organic electroluminescence devices which have on a substrate the luminous layer pinched by an anode plate and cathode It came to complete a header and this invention for the above-mentioned technical problem being solvable by forming the hole injection layer which consists of an aromatic series diamine content polyether which contains an electronic receptiveness compound and has high T<sub>g</sub> between an anode plate and a luminous layer.

[0019]

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## EXAMPLE

[Example] Next, although the example of an experiment, the example of comparative experiments, an example, and the example of a comparison explain this invention still more concretely, this invention is not limited to the publication of the following examples, unless the summary is exceeded.

[0077] After ultrasonic cleaning and pure water performed the example of experiment 1 glass substrate by rinsing and isopropyl alcohol and the acetone performed desiccation, and UV / ozone washing with ultrasonic cleaning and desiccation nitrogen, the spin coat of the aromatic series diamine content polyether (; weight average molecular weight 9300; glass transition temperature 190 degrees C which consists of 100% of repeat units show in the number (I-1) of Table 1) compounded by the approach as stated above was carried out on the above-mentioned glass substrate on condition that the following.

[0078]

Solvent 1,2-dichloroethane coating liquid concentration 30 [mg/ml]

Spinner rotational frequency 2500 [rpm]

Spinner turnover time 25 [a second]

Desiccation conditions The uniform thin film of 30nm thickness was formed of the spin coat of - air-drying above during 90 minutes. When the ionization potential of this thin film sample was measured using the ultraviolet-rays electronic analysis apparatus (AC-1) by Riken Keiki Co., Ltd., the value of 5.23eV was shown.

[0079] About some electronic receptiveness compounds with which reduction potential is reported, an electron affinity is shown in Table 6. Moreover, a difference with the ionization potential of the above-mentioned aromatic series diamine content polyether is written together to Table 6.

[0080]

[Table 6]

	還元電位 [V vs. SCE]	電子親和力 [eV]	イオン化ポテンシャル -電子親和力 [eV]
C60	-0.44	3.86	1.37
p-クロラニル	-0.01	4.29	0.94
TCNQ	0.19	4.49	0.74
DDQ	0.51	4.81	0.52
TBPAH	1.06	5.36	-0.13

TCNQ : 7,7,8,8-Tetracyanoquinodimethane

DDQ : 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

TBPAH : Tris(4-bromophenyl)aminium hexachloroantimonate

[0081] DDQ of an electronic receptiveness compound was mixed to the example of experiment 2 aromatic-series diamine content polyether (it consists of 100% of repeat units shown in the number (I-1) of Table 1), and the spin coat was carried out on the glass substrate like the example 1 of an experiment on the following conditions.

[0082]

Solvent 1,2-dichloroethane I-1 30mgDDQ 2mg coating liquid concentration 30 [mg/ml]

Spinner rotational frequency 2500 [rpm]

Spinner turnover time 25 [a second]

Desiccation conditions The thin film which contains DDQ with 30nm uniform thickness 6% of the weight with the spin coat of - air-drying above during 90 minutes was formed. The result of having measured the absorption spectrum for a visible region of this thin film sample is shown in drawing 5. As shown in drawing 5, the transparent film was obtained in the light field.

[0083] Except having used the aromatic series diamine content polyether (; weight-average-molecular-weight 25100; glass transition temperature of 183 degrees C which consists of 100% of repeat units shown in the number

(I-23) of Table 3) compounded by the approach as stated above as an example of experiment 3 aromatic-series diamine content polyether, like the example 1 of an experiment, the spin coat was performed and the uniform thin film of 40nm thickness was formed on the glass substrate.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the typical sectional view showing an example of the gestalt of operation of the organic electroluminescence devices of this invention.

[Drawing 2] It is the typical sectional view showing other examples of the gestalt of operation of the organic electroluminescence devices of this invention.

[Drawing 3] It is the typical sectional view showing another example of the gestalt of operation of the organic electroluminescence devices of this invention.

[Drawing 4] It is the energy level diagram having shown the relation between ionization potential and an electron affinity.

[Drawing 5] It is the graph which shows the transparency spectrum in a part for the visible region of the thin film formed in the example 2 of an experiment, and the example 1 of comparative experiments.

[Description of Notations]

- 1 Substrate
- 2 Anode Plate
- 3 Hole Injection Layer
- 4 Electron Hole Transportation Layer
- 5 Luminous Layer
- 6 Electronic Transportation Layer
- 7 Cathode

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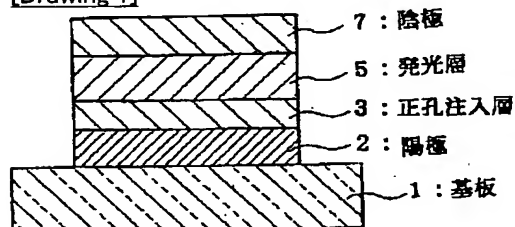
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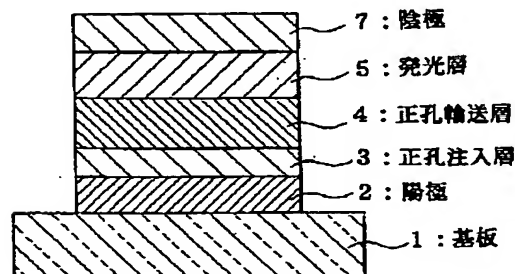
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## DRAWINGS

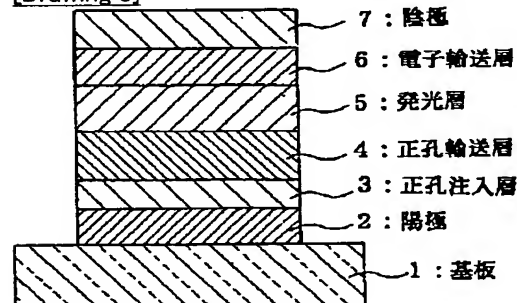
[Drawing 1]



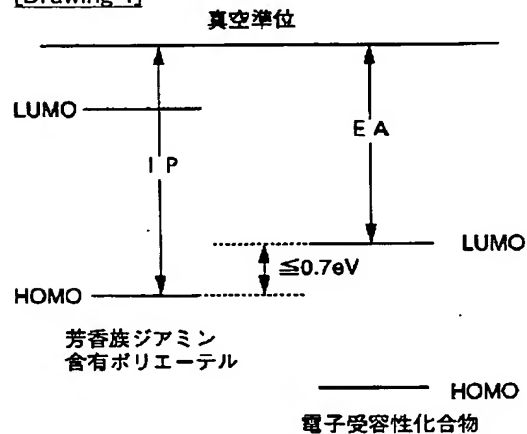
[Drawing 2]



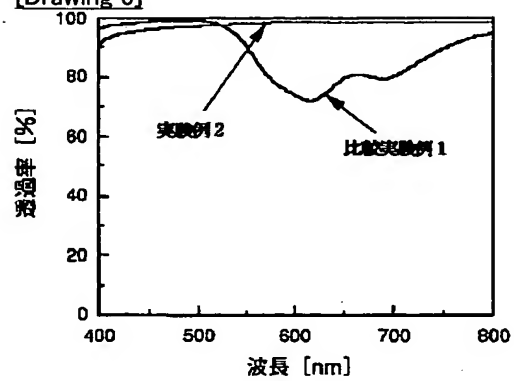
[Drawing 3]



[Drawing 4]



[Drawing 5]



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[Translation done.]